Solvent Extraction Behavior of 96Tc-TTA Complex

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Tris(acetylacetonato)technetium(III)($Tc(acac)_3$) has recently been synthesized.[1,2] However, no knowledge on the chemical properties of technetium(III, IV, V) β-diketonate complexes has been accumulated. In the present paper, the chemical behavior of thenoyltrifluoroacetonate(TTA) complexes of ^{96}Tc will be discussed by means of solvent extraction and silica gel chromatography methods.

Experimental

Carrier-free $^{96}TcO_4^-$ was prepared according to the method described in an earlier paper.[3] Either with sodium tetrahydroborate or with concentrated hydrochloric acid, $^{96}TcO_4^-$ was reduced to tri- and tetra-valent state in the presence of TTA and the synthesized TTA complexes were extracted into a benzene solution. Distribution ratio of ^{96}Tc was obtained by the back extraction in order to eliminate the chemical species which cannot participate in the distribution equilibrium. All the procedures were performed in a nitrogen gas atmosphere using a specially designed apparatus as shown in Fig. 1.

Results and Discussion

A separate experiment showed that distribution equilibrium was attained within 2.5 hours. Accordingly, the extraction time was chosen to be 3 hours.

Distribution ratio D which is defined as the ratio of the concentration of ^{96}Tc in the organic phase to that in the aqueous phase is obtained as both functions of pH and concentration of TTA.

In many extraction systems, distribution ratio is expressed as follows:

$$\log D = \log K + n\log [HA] + npH \qquad (1)$$

in which n is the charge on the metal ion and HA is the chelating agent. K is called the extraction constant. It was found, however, that Eq. (1) cannot be applied directly to the present system.

In order to analyze precisely the distribution curves, the chromatographic behavior of ^{96}Tc species in the both phases was examined. This showed that no detectable amount of pertechnetate is present in the aqueous phase. On the other hand, the extractable species are formed to be $^{96}Tc(tta)_3$ and $^{96}Tc(tta)_4$ by means of a silica gel chromatography. The finding that $^{96}Tc(tta)_3$ is formed even in the reduction of hydrochloric acid is contrasted to the results of earlier studies.[4,5] $^{96}Tc(tta)_3$ is substitution-inert similar to $Tc(acac)_3$,[1] so that the distribution ratio is high and independent of pH.

In the aqueous phase, chemical species of Tc(IV) is highly complicated and it is appreciably hydrolyzed to TcO^{2+} even at pH 1.[6]

After elimination of the contribution of $Tc(tta)_3$ distribution curves was reconstructed as is shown in Fig. 2. The overall extraction mechanism of Tc(IV) species will thus be expressed by the following equation.

$$D = \frac{D_0 \beta_4 [tta^-]_a^4}{1 + \Sigma \beta_n [tta^-]_a^n + \Sigma K_m \cdot \frac{K_W^m}{[H^+]^m}} \qquad (2)$$

Where $D_0 = [Tc(tta)_4]_o / [Tc(tta)_4]_a$ $\qquad \beta_n = [Tc(tta)_n^{(4-n)+}] / ([Tc^{4+}][tta^-]^n)$

$K_m = [Tc(OH)_m^{(4-m)+}] / ([Tc^{4+}][OH^-]^m)$ $\qquad K_W = [H^+][OH^-]$

If the hydrolysis of Tc(IV) is ignored, a plot of log D against -log $[tta^-]$ should be a single curve without respect to the concentration of TTA. Figure 2 shows, however, that there is evidently an effect of the hydrolysis of Tc(IV). Although attempts to determine the parameters in Eq. (2) have not yet been successful, it can be said at least that the extraction mechanism of Tc(IV)-TTA complex proposed by Levin et al.[7] should be reexamined.

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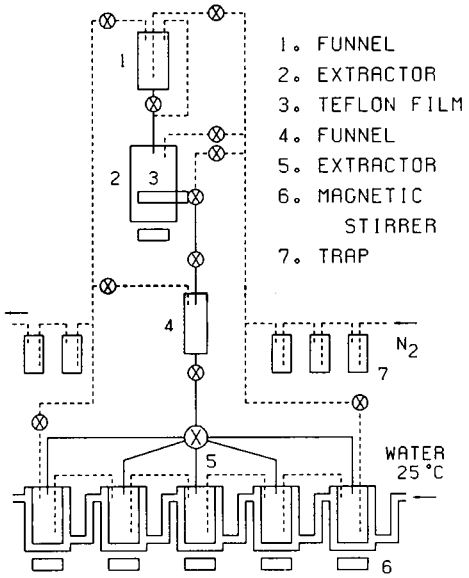

Fig. 1. Extraction apparatus.

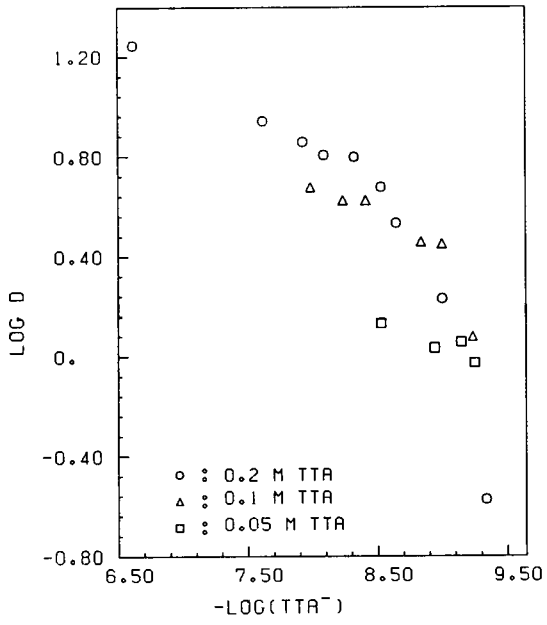

Fig. 2. Distribution behavior of ^{96}Tc(IV)-TTA complex at 25°C.